BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/20870 A1

(51) International Patent Classification[7]: C23C 16/40

(21) International Application Number: PCT/US01/28061

(22) International Filing Date:
7 September 2001 (07.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/658,654 8 September 2000 (08.09.2000) US

(71) Applicant: **APPLIED MATERIALS, INC.** [US/US]; P.O. Box 450A, Santa Clara, CA 95052 (US).

(72) Inventors: **URDAHL, Randall, S.**; 1361 Ormonde Way, Mountain View, CA 94043 (US). **NARWANKAR, Pravin, K.**; 392 Waverly Street, Sunnyvale, CA 94087 (US). **ATHREYA, Shankarrram, A.**; 415 S. Bernardo Avenue #214, Sunnyvale, CA 94086 (US). **SINENSKY, Asher, K.**; 1701 Woolsey Street, Berkeley, CA 94703 (US). **MENDOZA, Andrea, M.**; 2725 Alma Street, Palo Alto, CA 94306 (US).

(74) Agents: **BERNADICOU, Michael, A.** et al.; Blakely, Sokoloff, Taylor & Zafman LLP, 7th Floor, 12400 Wilshire Boulevard, Los Angeles, CA 90025 (US).

(81) Designated States *(national)*: CN, JP, KR.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/20870 A1

(54) Title: CHEMICAL VAPOR DEPOSITION OF TANTALUM OXIDE USING OXYGEN-FREE LIQUID PRECURSORS

(57) Abstract: The present invention provides a method of depositing tantalum pentaoxide, comprising the step of vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature of less than about 180 °C, a deposition temperature of less than about 500 °C and a deposition pressure of less than about 96 Torr such that the tantalum pentaoxide is integrated into the MIM capacitor. Also provided is a method of depositing tantalum pentaoxide, comprising the step of vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature from about 100 °C to about 180 °C, a deposition temperature from about 300 °C to about 500 °C and a deposition pressure from about 0.5 Torr to about 96 Torr, such that the tantalum pentaoxide is integrated into the MIM capacitor.

CHEMICAL VAPOR DEPOSITION OF TANTALUM OXIDE USING OXYGEN-FREE LIQUID PRECURSORS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to the fields of applied physics and chemical vapor deposition of dielectric films. More specifically, the present invention relates to a method of low temperature deposition of a tantalum oxide dielectric film using a liquid precursor during metal organic chemical vapor deposition.

Description of the Related Art

The current trend toward higher density memories in DRAM capacitors together with the concomitant shrinking of device geometries to 0.35 μm or less and decreases in cell size

requires better dielectric films for these structures. As the next generation DRAM technology evolves, it will become necessary to use three-dimensional capacitors despite the thin capacitor dielectrics employed. These DRAM devices require a high capacitance density and a small leakage current, even when the dielectric film is thin.

In metal-insulator-metal capacitors, tantalum pentaoxide (Ta_2O_5) is a preferred material for capacitor dielectrics. Although other dielectric films have higher *k*-values than tantalum pentaoxide (*k*~25 for amorphous Ta_2O_5), they can be more difficult to integrate in device structures than tantalum pentaoxide. Regardless, with standard processing techniques, tantalum pentaoxide dielectric thin films are still difficult to deposit, e.g., control the dielectric composition such that the deposited film has high capacitance and low leakage current densities.

If the films are being used as capacitor dielectrics for DRAM applications, it is advantageous to use a chemical vapor deposition process (CVD), preferably using a metal-organic precursor. The use of liquid-source metal-organic precursors in the CVD of dielectric films provides a means to deposit high quality thin-films with excellent step-coverage. In current MOCVD applications, tantalum pentaoxide films are deposited in an oxygen ambient using either TAETO or TAT-DMAE as the liquid precursor.

As-deposited tantalum pentaoxide films, i.e., not yet annealed, are typically characterized by a high density of compositional and structural defects. These defects are incorporated in the film during the deposition process, and result in a relatively high leakage current density compared to that for an annealed film. As a result, tantalum pentaoxide films generally require an additional oxidation (i.e. annealing) step, to improve the film stoichiometry and reduce the defect density. However, an oxidizing environment can also cause the formation of parasitic oxides or oxy-nitrides at the electrode interface, which tend to lower the capacitance density. Thus in order to optimize the electrical performance of tantalum pentaoxide, both the deposition and anneal conditions must be carefully controlled to lower the defect density in the film while simultaneously minimizing the formation of any interfacial oxides.

The prior art is deficient in the lack of an effective method to rapidly deposit (>0.5-1 Angstrom/second) tantalum pentaoxide at low temperatures and pressures. The metal-organic chemical vapor deposition of tantalum pentaoxide dielectric films by direct injection of an oxygen-free liquid precursor fulfills this long-standing need and desire in the art.

SUMMARY OF THE INVENTION

One embodiment of the present invention is a method of depositing tantalum pentaoxide, comprising the step of vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature of less than about 180°C, a deposition temperature of less than about 500°C and a deposition pressure of less than about 96 Torr such that the tantalum pentaoxide is integrated into the MIM capacitor.

Another embodiment of the present invention is a method of depositing tantalum pentaoxide, comprising the step of vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature from about 100°C to about 180°C, a deposition temperature from about 300°C to about 500°C and an atmospheric pressure from about 0.5 Torr to about 96 Torr, such that the tantalum pentaoxide is integrated into the MIM capacitor.

Other and further aspects, features, and advantages of the present invention will be apparent from the following description of the presently preferred embodiments of the invention given for the purpose of disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

So that the matter in which the above-recited features, advantages and objects of the invention, as well as others which will become clear, are attained and can be understood in detail, more particular descriptions of the invention briefly summarized above may be had by reference to certain embodiments thereof which are illustrated in the appended drawings. These drawings form a part of the specification. It is to be noted, however, that the appended drawings illustrate preferred embodiments of the invention and therefore are not to be considered limiting in their scope.

Figure 1 depicts the Arrhenius plot for tantalum oxide deposition using ethylimino ethyl(CN) tris(diethylamido)tantalum (**Figure 1A**) and butylimino tris(diethylamino) tantalum (**Figure 1B**). For tantalum pentaoxide deposition using butylimino tris(diethylamino) tantalum, vaporizer temperature was 120°C, pressure was 4Torr and the flow rate was 75 mg/min.

Figure 2 depicts the deposition rate of tantalum oxide (Ta_2O_5) versus ethylimino ethyl(CN) tris(diethylamido)tantalum (**EITDET-c**) flow rate at 4 Torr and 400 °C. The vaporizer temperatures are ~100 °C, ~125 °C and ~150 °C.

Figure 3 depicts the deposition rate of tantalum oxide (Ta_2O_5) versus total pressure at a flow rate of 50 mg/min of EITDET precursor and a wafer temperature of 400 °C. The vaporizer temperatures are 100 °C and 150 °C.

Figure 4 depicts the deposition rate of tantalum oxide (Ta_2O_5) on ~20 Å plasma oxide and native oxide versus total pressure at a flow rate of 100 mg/min. of EITDET-c precursor, a vaporizer temperature of 150 °C and a calibrated wafer temperature of 400°C.

Figure 5 depicts the effect of the TBTDET flow rate on the deposition rate. The vaporizer temperature is 180°C, wafer temperature is 400°C and the chamber pressure is at 4 Torr.

Figure 6 depicts the effect of the process pressure on the deposition rate. The vaporizer temperature is 120°C, wafer temperature is 400°C and the TBTDET flow rate is 75 mg/min.

Figure 7 depicts the variation of oxygen flow and oxygen/nitrogen ratio during a TBT-DET process splits for RBS data (**Fig. 7A**) and XPS data (**Fig. 7B**). depicts the percentage elemental concentration of tantalum, oxygen, nitrogen, and carbon in an as-deposited tantalum pentaoxide film grown using the TBTDET precursor. The analytical methods used to obtain the atomic concentration data are Rutherford back-scattering

spectroscopy (RBS) (**Fig. 7A**) and X-ray photoelectron spectroscopy (XPS) (**Fig. 7B**).

DETAILED DESCRIPTION OF THE INVENTION

One object of the present invention is a method of depositing tantalum pentaoxide, comprising the step of vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature of less than about 180°C, a deposition temperature of less than about 500°C and a deposition pressure of less than about 96 Torr such that the tantalum pentaoxide is integrated into the MIM capacitor. The oxygen-free liquid precursor is delivered via direct injection for use in a metalorganic chemical vapor deposition applicaton. A representative example of the oxygen-free liquid precursors is a 70:30 mixture by weight of ethylimino tris(diethylamino) tantalum and ethylimino ethyl(CN) tris(diethylamido)tantalum (EITDET-c). Other examples include ethylimino tris(diethylamino) tantalum (EITDET), and butylimino tris(diethylamino) tantalum (TBTDET). Additionally, a vaporizer temperature from about 100°C to about 180°C, a deposition temperature from about 300°C to about 500°C and a deposition pressure from about 0.5 Torr to about 96 Torr are selected.

Another embodiment, the present invention is directed a method of depositing tantalum pentaoxide, comprising

the step of vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature from about 100°C to about 180°C, a deposition temperature from about 300°C to about 500°C and an atmospheric pressure from about 0.5 Torr to about 96 Torr, such that the tantalum pentaoxide is integrated into the MIM capacitor.

The oxygen-free liquid precursor is delivered via direct injection for use in a metalorganic chemical vapor deposition applicaton. A representative example of the oxygen-free liquid precursors is a 70:30 mixture by weight of ethylimino tris(diethylamino) tantalum and ethylimino ethyl(CN) tris(diethylamido)tantalum (EITDET-c). Other representative examples include ethylimino tris(diethylamino) tantalum (EITDET) and butylimino tris(diethylamino) tantalum (TBTDET).

Tantalum pentaoxide dielectric films can be deposited at a low temperature, i.e., less than about 450° using an oxygen-free liquid precursor. The critical parameters in this process are the selection of the vaporizer temperature, deposition temperature and total deposition pressure. Some examples of these compounds are EITDET-c which is a 70:30 mixture by weight of ethylimino tris(diethylamino) tantalum and ethylimino ethyl(CN)tris(diethylamido) tantalum, tertiary-butylimino tris(diethylamino) tantalum (TBTDET) and ethylimino tris(diethylamino) tantalum (EITDET). It should be expected by one having ordinary skill in this art that any other oxygen-free

tantalum-containing metal-organic precursor would deposit tantalum pentaoxide films in a similar manner as under the same conditions as used for TBTDET, EITDET and EITDET-c.

High rates of tantalum pentaoxide deposition in an oxidizing ambient are obtained over a temperature range of from about 300°C to about 500°C for total pressures from about 0.5 Torr to 96 Torr. This rate of deposition is approximately 10 times faster than that achieved using tantalum pentaethoxide (TAETO) under comparable conditions. Furthermore, the deposition rate is enhanced if the liquid precursor is vaporized using the direct liquid injection method at temperatures from about 100°C to about 180°C.

The following examples are given for the purpose of illustrating various embodiments of the invention and are not meant to limit the present invention in any fashion.

EXAMPLE 1

Arrhenius studies of EITDET-c and TBTDET

The deposition temperature is varied for both EITDET-c and TBTDET precursors to determine the temperature dependence of the deposition rate using Arrhenius plots ($\log_{10}$ deposition rate vs. 1/T). Arrhenius plots are used to understand the reaction kinetics and thus determine the temperature

sensitivity of the CVD process. The Arrhenius plot for EITDET-c shows an activation energy (E_a) of 1.07eV (Fig. 1A) whereas the Arrhenius plot for TBTDET shows an activation energy more than twice that of EITDET-c at 2.69eV.

EXAMPLE 2

Deposition characteristics of tantalum pentaoxide dielectric films using EITDET-c

EITDET-c flow rate is a variable in the deposition rate of tantalum pentaoxide films. Figure 2 examines the effect of increasing the EITDET-c flow rate on the deposition rate of these films at vaporization temperatures of ~100°C, ~125°C and ~150°C. Chamber pressure is 4 Torr and the deposition temperature is 400°C. The deposition rate of tantalum pentaoxide is significantly increased as EITDET-c flow rates increase at higher vaporizer temperatures. At a 50 mg/minute flow of EITDET-c with a vaporizer temperature of ~150°C, the deposition rate is ~70 Å/minute, a 20% increase over deposition rate with a vaporizer temperature of ~100°C. Additionally, at the lower vaporization temperatures the deposition rate levels off at a flow rate of 40 mg/minute of EITDET-c.

Using this optimum flow rate of 50 mg/min. EITDET-c, Figure 3 depicts the change in deposition rate of tantalum pentaoxide as a function of total pressure for vaporizer

temperatures of 100°C and 150°C. Again the higher vaporization temperature yields better deposition of films as total pressure increases. However, even for optimum conditions, the deposition rate appears to decline as pressure increases.

Figure 4 examines the deposition rate of tantalum pentaoxide films on ~20Å plasma oxide and on native oxide as a function of total pressure using a flow rate of 100 mg/min of EITDET-c vaporized at 150°C. Under these conditions, the deposition rate increases dramatically for pressures up to about 32 Torr for deposition on native oxide. However on ~20Å plasma oxide, deposition levels off at 32 Torr and even decreases as the total pressure increases. Therefore, vaporization temperature and total pressure can be tuned to achieve the desired deposition rate.

EXAMPLE 3

Deposition characteristics of tantalum pentaoxide dielectric films using TBTDET

TBTDET is also an oxygen-free tantalum containing liquid precursor used for the deposition of tantalum pentaoxide films. Figure 5 examines the effect of the TBTDET flow rate on the deposition rate of tantalum pentaoxide films. TBTDET is vaporized at a temperature of 180°C with a wafer temperature of 400°C and a chamber pressure of 4 Torr. The deposition rate at 12 Torr is significantly greater than that at 4 Torr; i.e., 110Å/min.

as compared to about 55Å/min., for a flow rate of 100 mg/min. In fact at 4 Torr of pressure the deposition rate levels off when the flow rate reaches about 55 mg/min.

Figure 6 depicts the variation of deposition rate with process pressure for a flow rate of 75 mg/min. of TBTDET vaporized at a temperature of 120°C and a wafer temperature of 400°C. The deposition rate is seen to increase almost linearly over the range of 2 to 32 Torr.

The percentage elemental concentration of tantalum, oxygen, nitrogen, and carbon atoms in the as-deposited tantalum pentaoxide film is plotted in Figures 7A and 7B as a function of the p[oxidizer (O_2 or N_2O)] / p[nitrogen] partial pressure ratio and oxidizer flow rate. These films were deposited using TBTDET as the liquid precursor, and the % atomic concentrations give an indication as to the composition of the film (note that for a perfectly stoichiometric Ta_2O_5 film, one would expect to see 28.6% tantalum and 71.4% oxygen). The % atomic concentrations were measured using both Rutherford back-scattering spectroscopy (RBS) (Fig. 7A) and X-ray photoelectron spectroscopy (XPS) (Fig. 7B).

As is seen in Figures 7A and 7B, there is a significant concentration of atomic nitrogen and carbon incorporated in the as-deposited films. It is also seen that the relative % atomic concentrations of tantalum, oxygen, carbon, and nitrogen vary with relative amounts of oxygen (nitrous oxide) and nitrogen

used during the deposition process. This data is crucial in determining the type of annealing process required to increase the oxygen content in the film, while simultaneously reducing the levels of residual carbon and nitrogen.

Any patents or publications mentioned in this specification are indicative of the levels of those skilled in the art to which the invention pertains. These patents and publications are herein incorporated by reference to the same extent as if each individual publication was specifically and individually indicated to be incorporated by reference.

One skilled in the art will readily appreciate that the present invention is well adapted to carry out the objects and obtain the ends and advantages mentioned, as well as those inherent therein. It will be apparent to those skilled in the art that various modifications and variations can be made in practicing the present invention without departing from the spirit or scope of the invention. Changes therein and other uses will occur to those skilled in the art which are encompassed within the spirit of the invention as defined by the scope of the claims.

WHAT IS CLAIMED IS:

1. A method of depositing tantalum pentaoxide, comprising the step of:

vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature of less than about 180°C, a deposition temperature of less than about 500°C and a deposition pressure of less than about 96 Torr such that the tantalum pentaoxide is integrated into the MIM capacitor.

2. The method of claim 1, wherein the oxygen-free liquid precursor is delivered by direct injection for use during a metalorganic chemical vapor deposition application.

3. The method of claim 1, wherein the oxygen-free liquid precursor is a 70:30 mixture by weight of ethylimino tris(diethylamino) tantalum and ethylimino ethyl(CN) tris(diethylamido)tantalum.

4. The method of claim 1, wherein the oxygen-free liquid precursor is selected from the group consisting of ethylimino tris(diethylamino) tantalum and butylimino tris(diethylamino) tantalum.

5. The method of claim 1, wherein the vaporizer temperature is from about 100°C to about 180°C.

6. The method of claim 1, wherein the deposition temperature is from about 300°C to about 500°C.

7. The method of claim 1, wherein the deposition pressure is from about 0.5 Torr to about 96 Torr.

8. A method of depositing tantalum pentaoxide, comprising the step of :

vapor-depositing the tantalum pentaoxide from an oxygen-free liquid precursor and under process conditions comprising a vaporizer temperature from about 100°C to about 180°C, a deposition temperature from about 300°C to about 500°C and a deposition pressure from about 0.5 Torr to about 96 Torr, such that the tantalum pentaoxide is integrated into the MIM capacitor.

9. The method of claim 8, wherein the oxygen-free liquid precursor is delivered by direct injection for use during a metalorganic chemical vapor deposition application.

10. The method of claim 8, wherein the oxygen-free liquid precursor is a 70:30 mixture by weight of ethylimino tris(diethylamino) tantalum and ethylimino ethyl(CN) tris(diethylamido)tantalum.

11. The method of claim 8, wherein the oxygen-free liquid precursor is selected from the group consisting of ethylimino tris(diethylamino) tantalum and butylimino tris(diethylamino) tantalum.

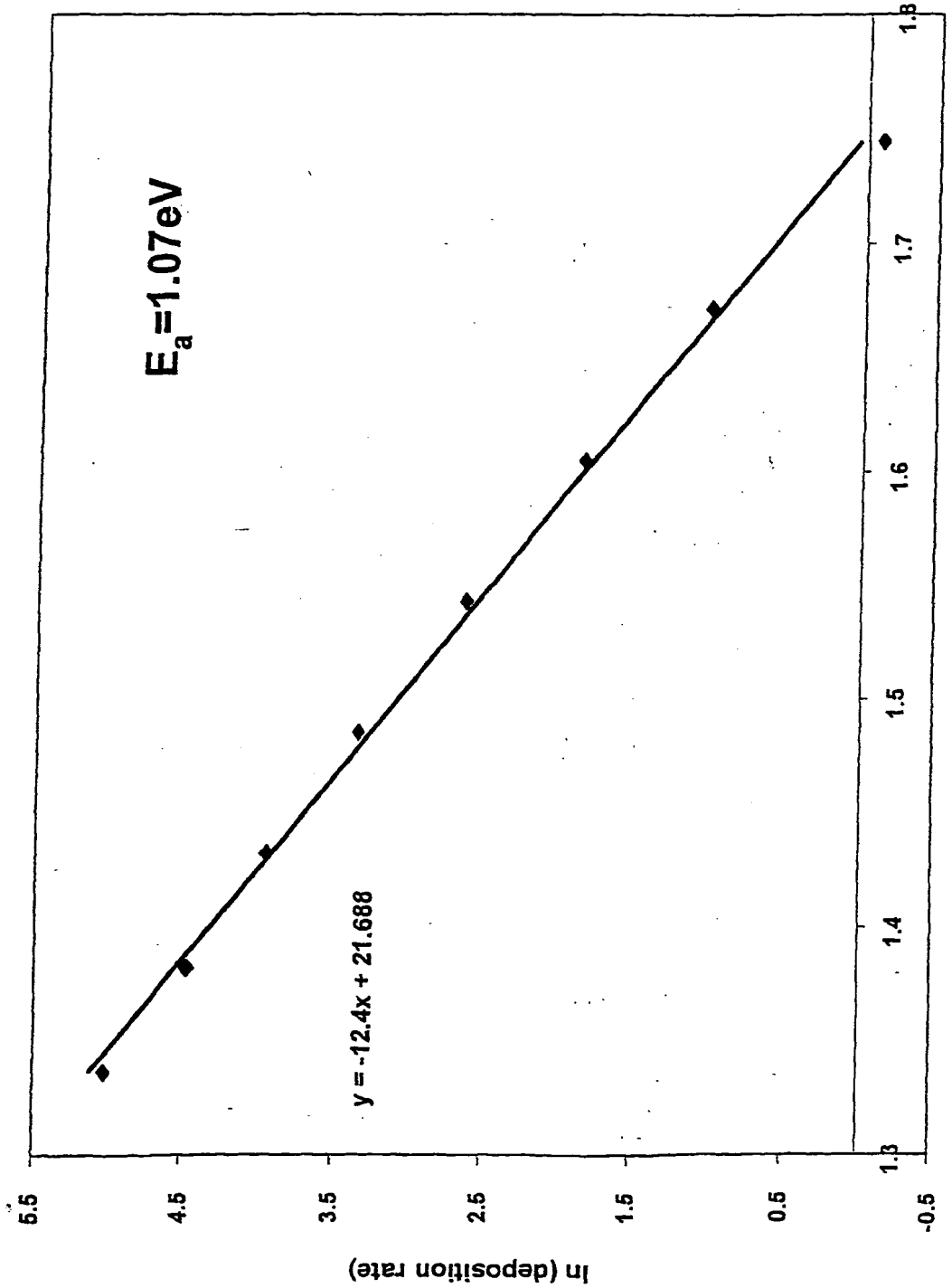

Fig. 1A

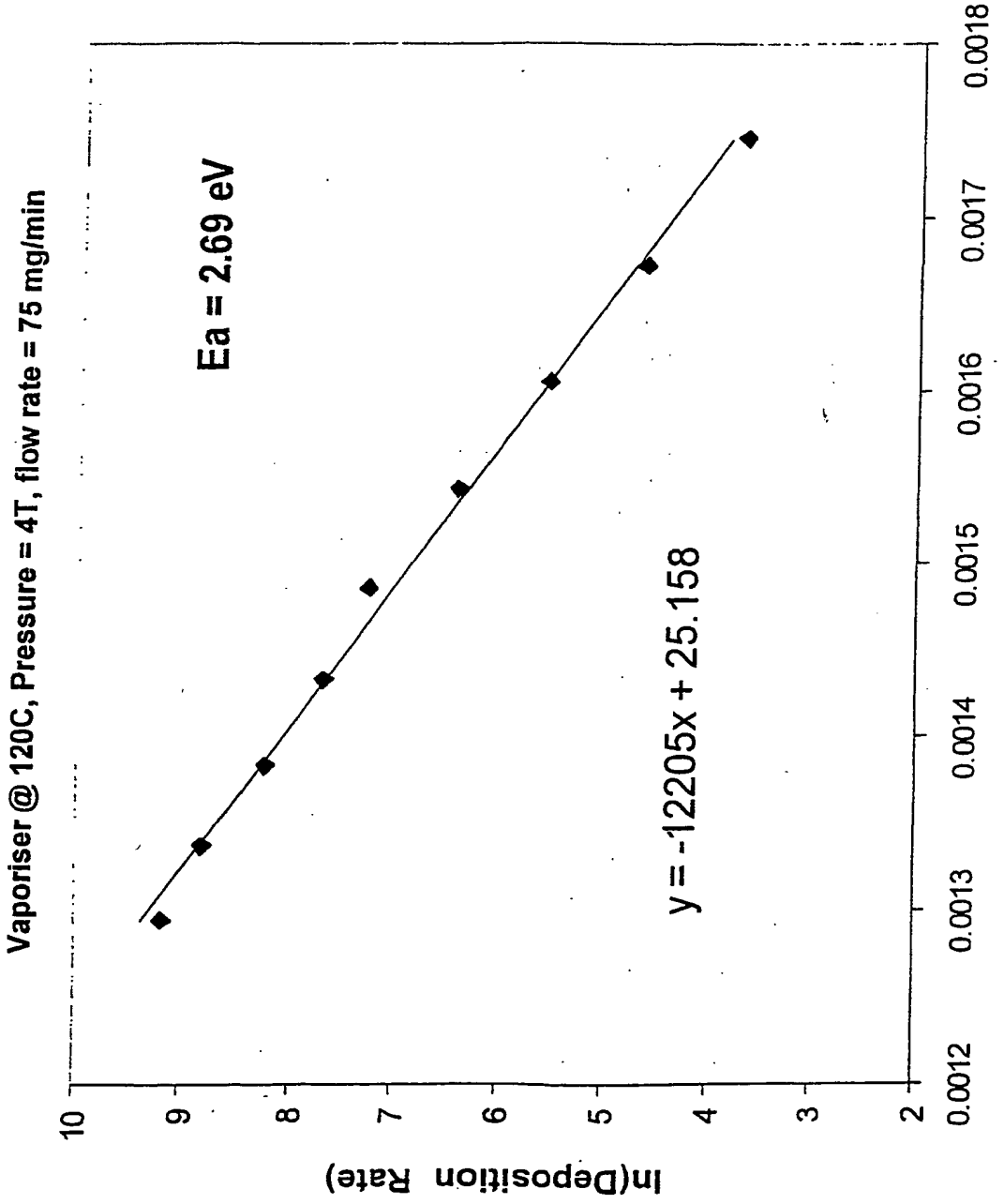
Vaporiser @ 120C, Pressure = 4T, flow rate = 75 mg/min
Ea = 2.69 eV
y = -12205x + 25.158
ln(Deposition Rate)
1/Temp, 1/K
10
9
8
7
6
5
4
3
2
0.0012
0.0013
0.0014
0.0015
0.0016
0.0017
0.0018

Fig. 1B

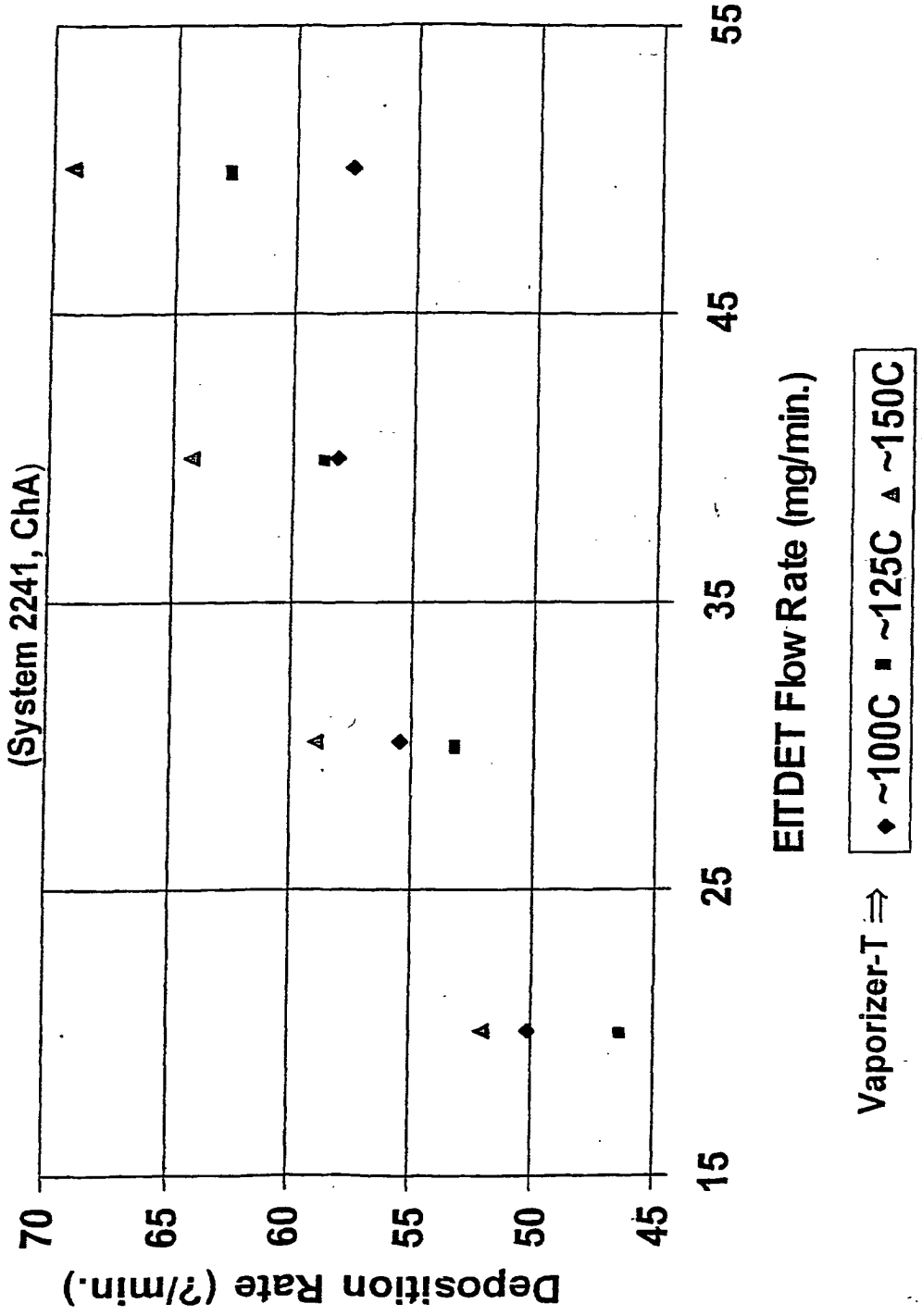

Fig. 2

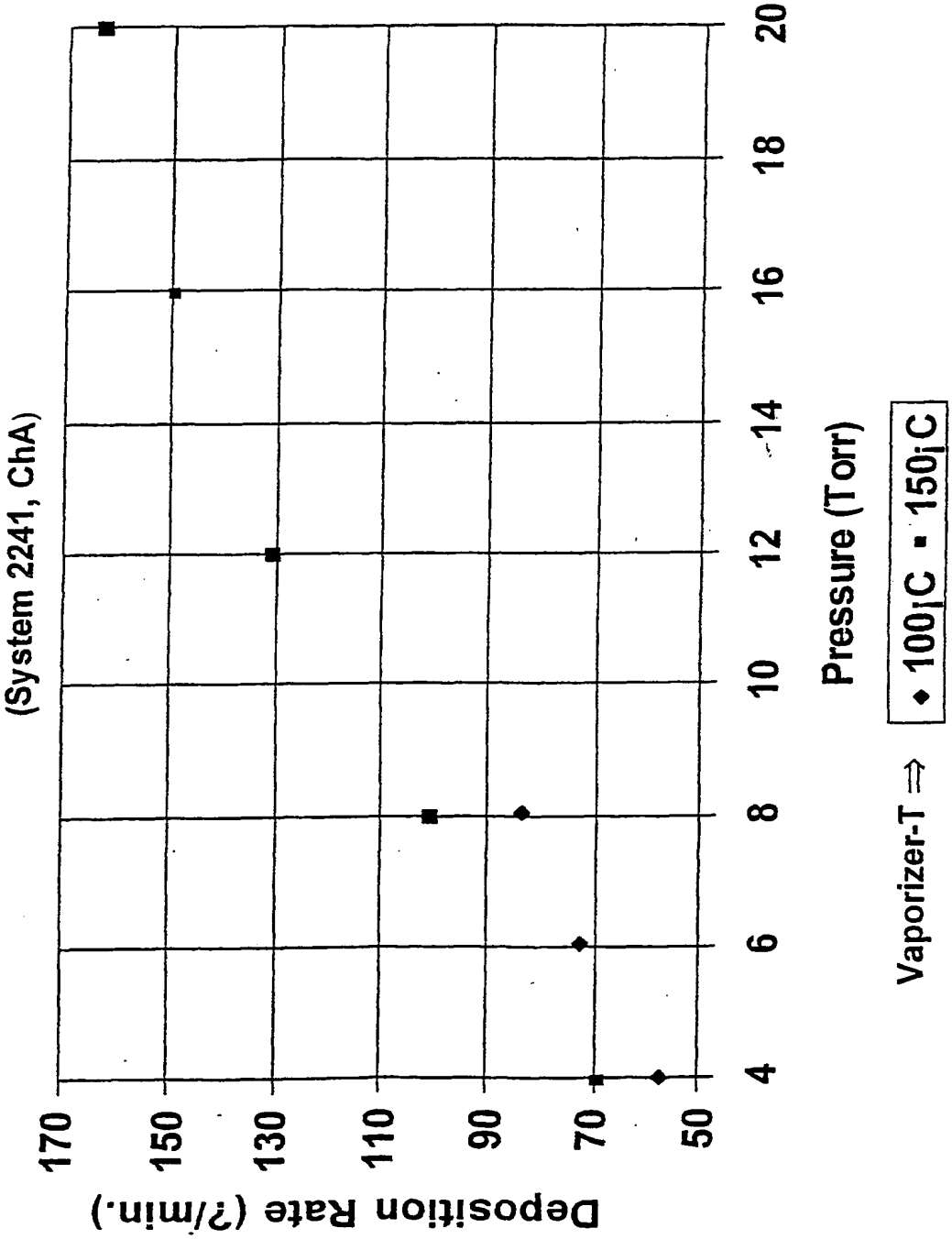
Deposition Rate (?/min.)
170
150
130
110
90
70
50
(System 2241, ChA)
4
6
8
10
12
14
16
18
20
Pressure (Torr)
Vaporizer-T ⇒
◆ 100¡C ▪ 150¡C

Fig. 3

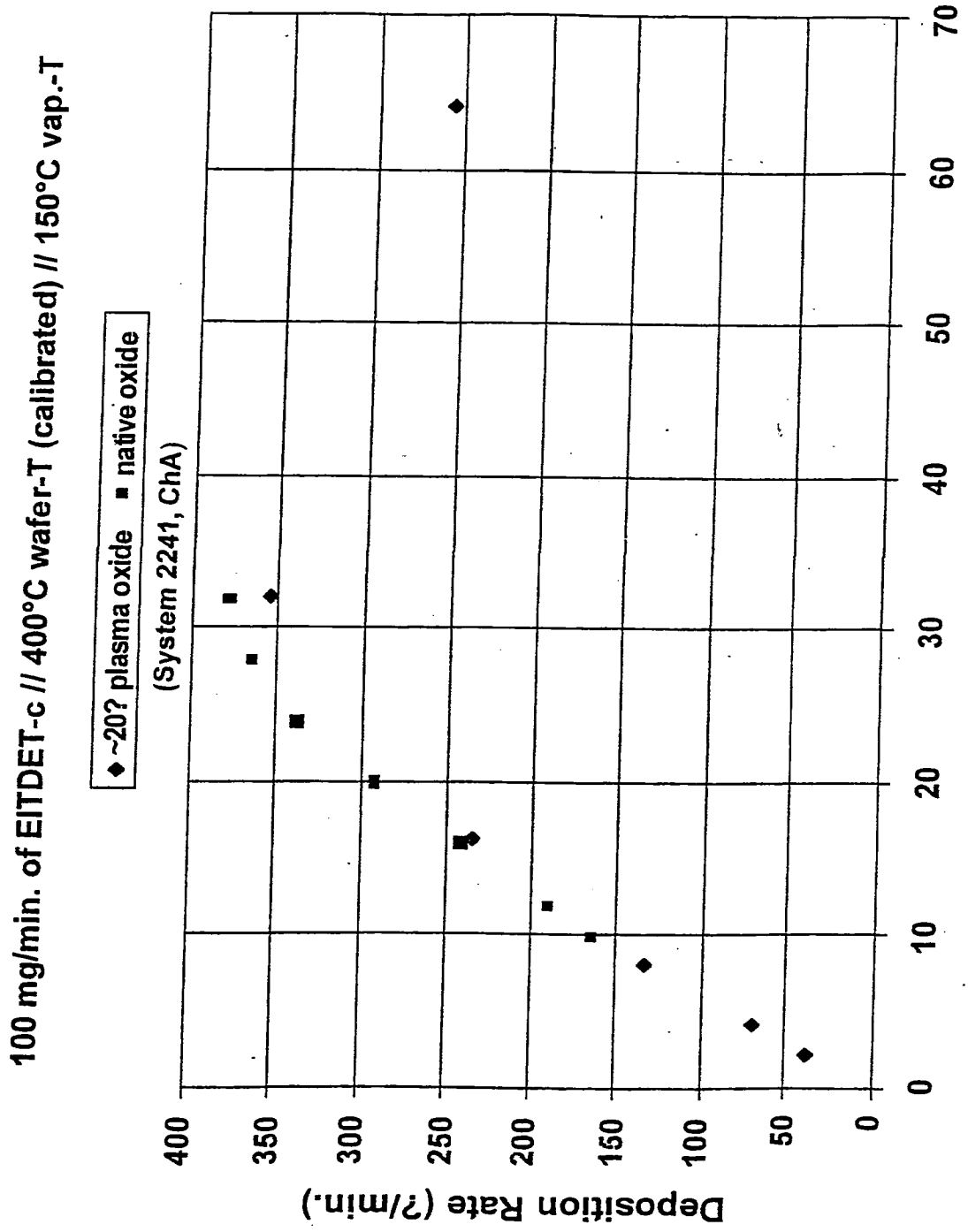

Fig. 4

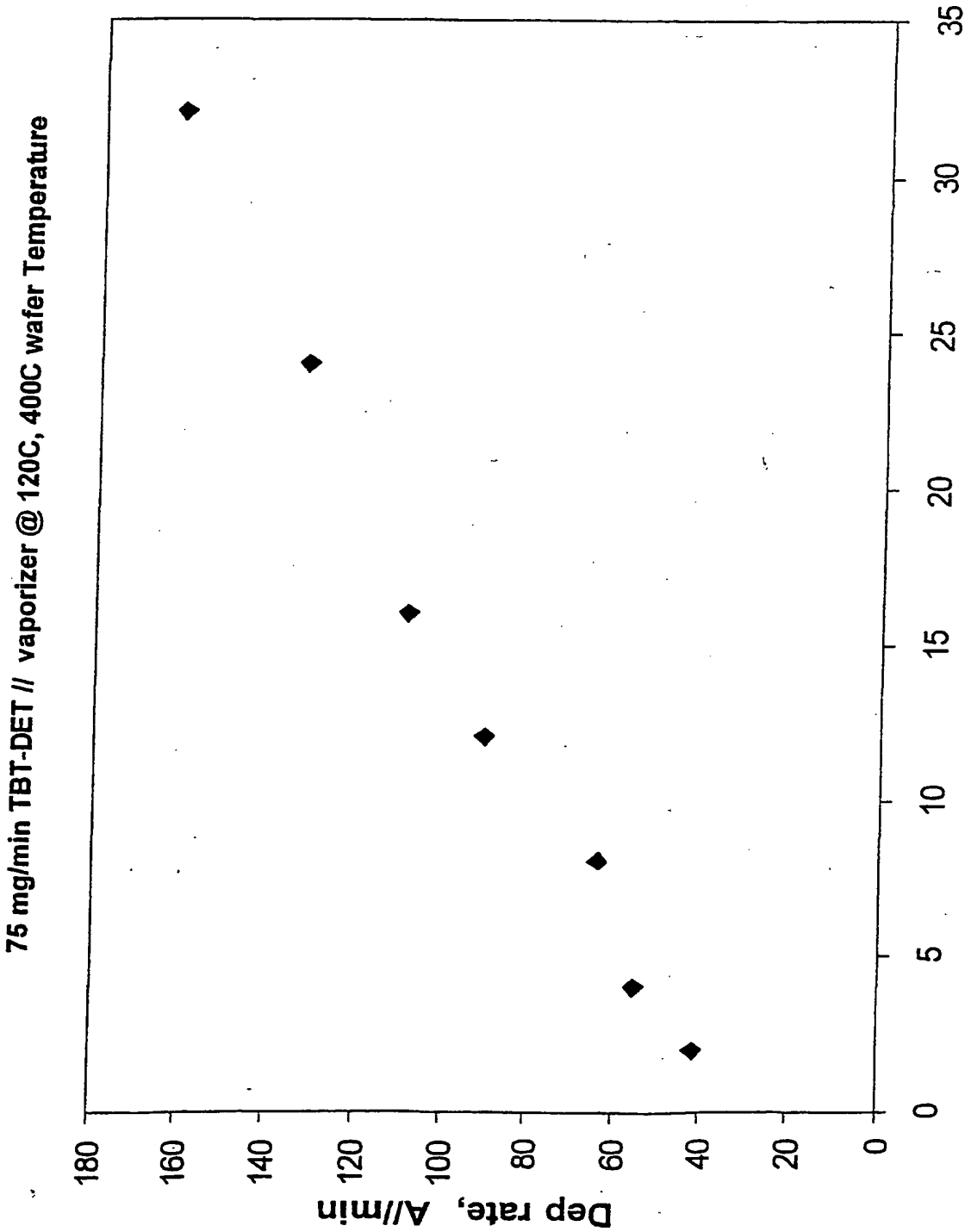
75 mg/min TBT-DET // vaporizer @ 120C, 400C wafer Temperature
Dep rate, A//min
0
20
40
60
80
100
120
140
160
180
Process Pressure, T
0
5
10
15
20
25
30
35

Fig. 5

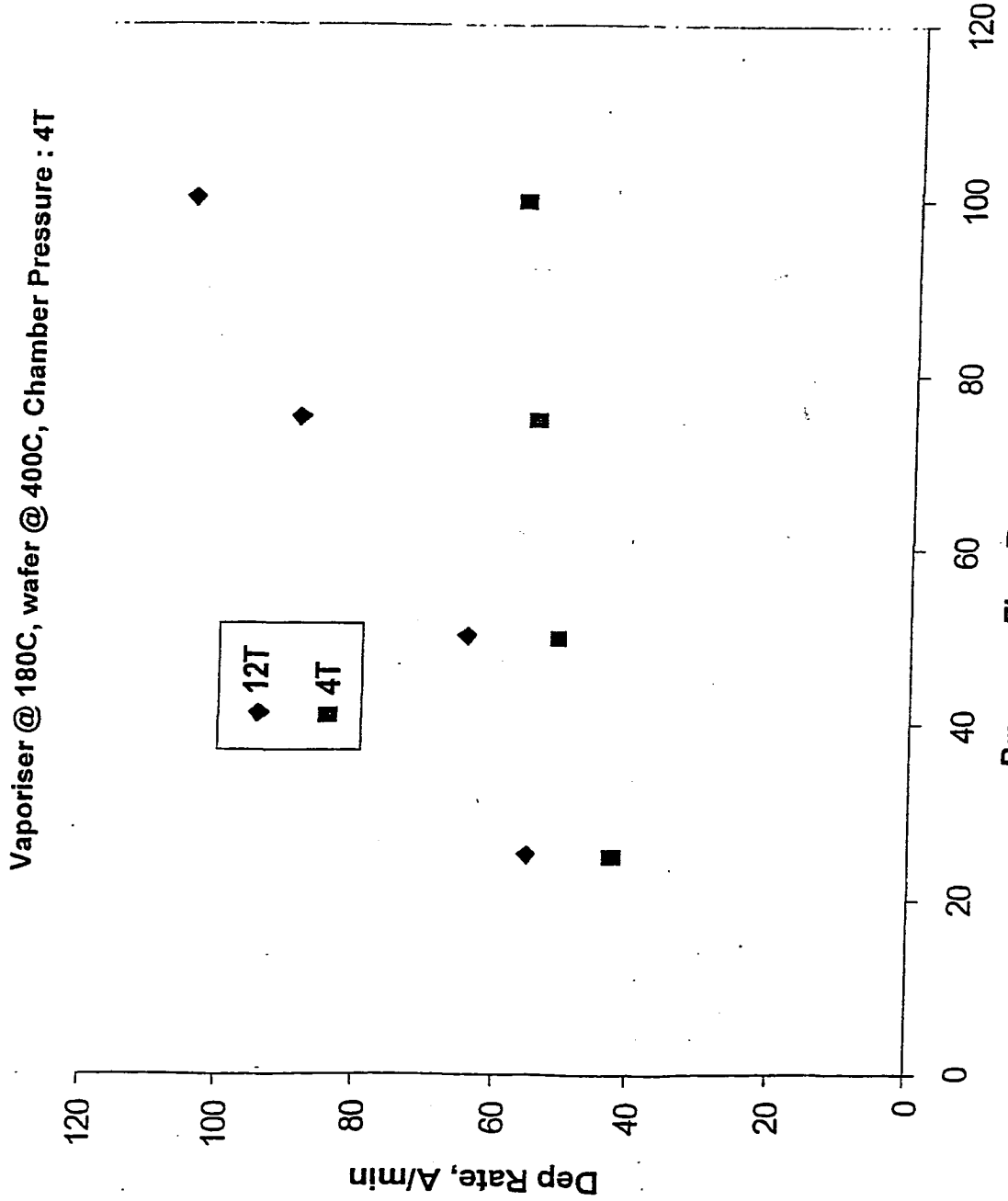

Fig. 6

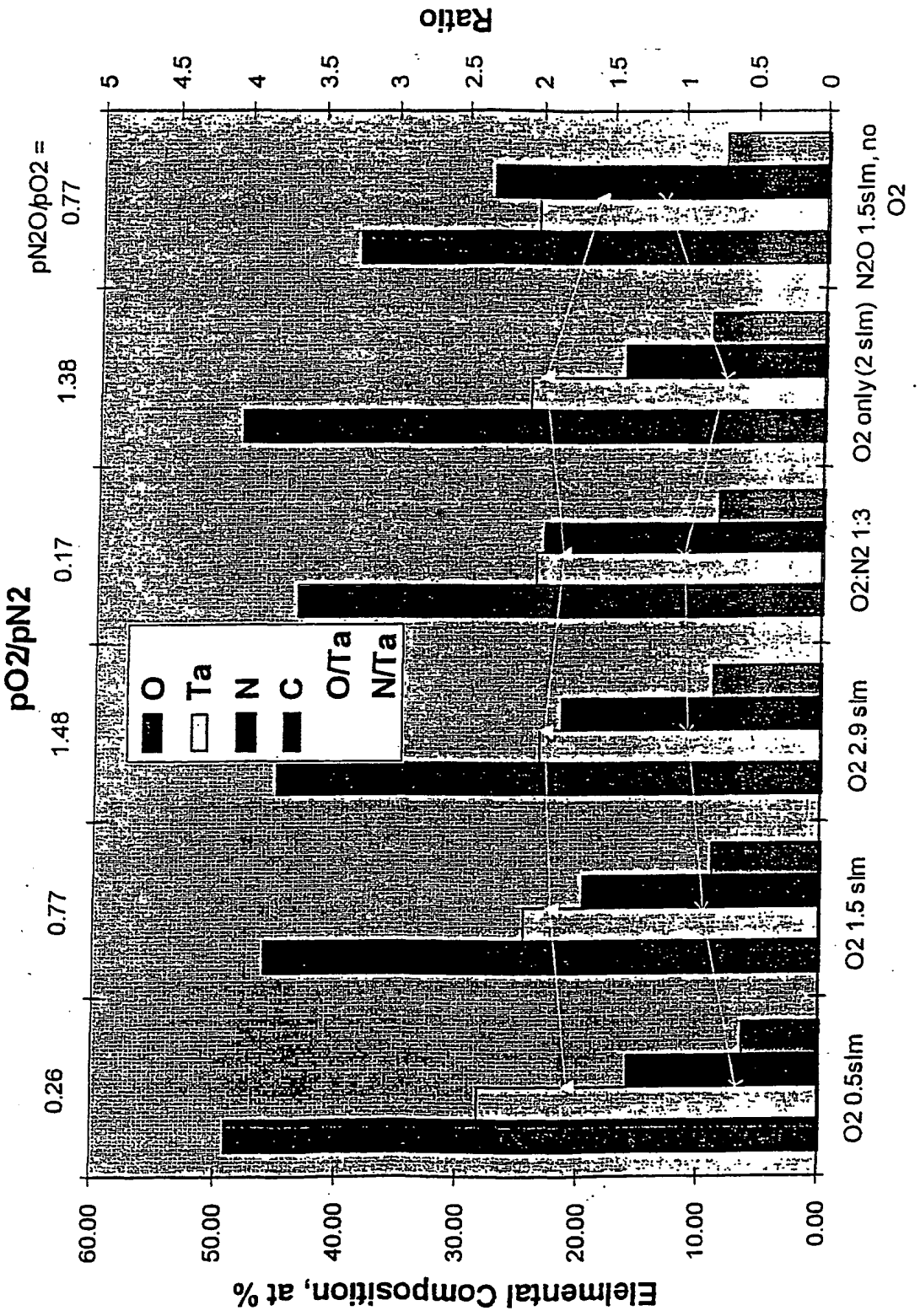
Elemental Composition, at %
Ratio
pO2/pN2
pN2O/pO2 =
O
Ta
N
C
O/Ta
N/Ta
0.26
0.77
1.48
0.17
1.38
0.77
O2 0.5slm
O2 1.5 slm
O2 2.9 slm
O2:N2 1:3
O2 only(2 slm)
N2O 1.5slm, no O2
Process Split conditions

Fig. 7A

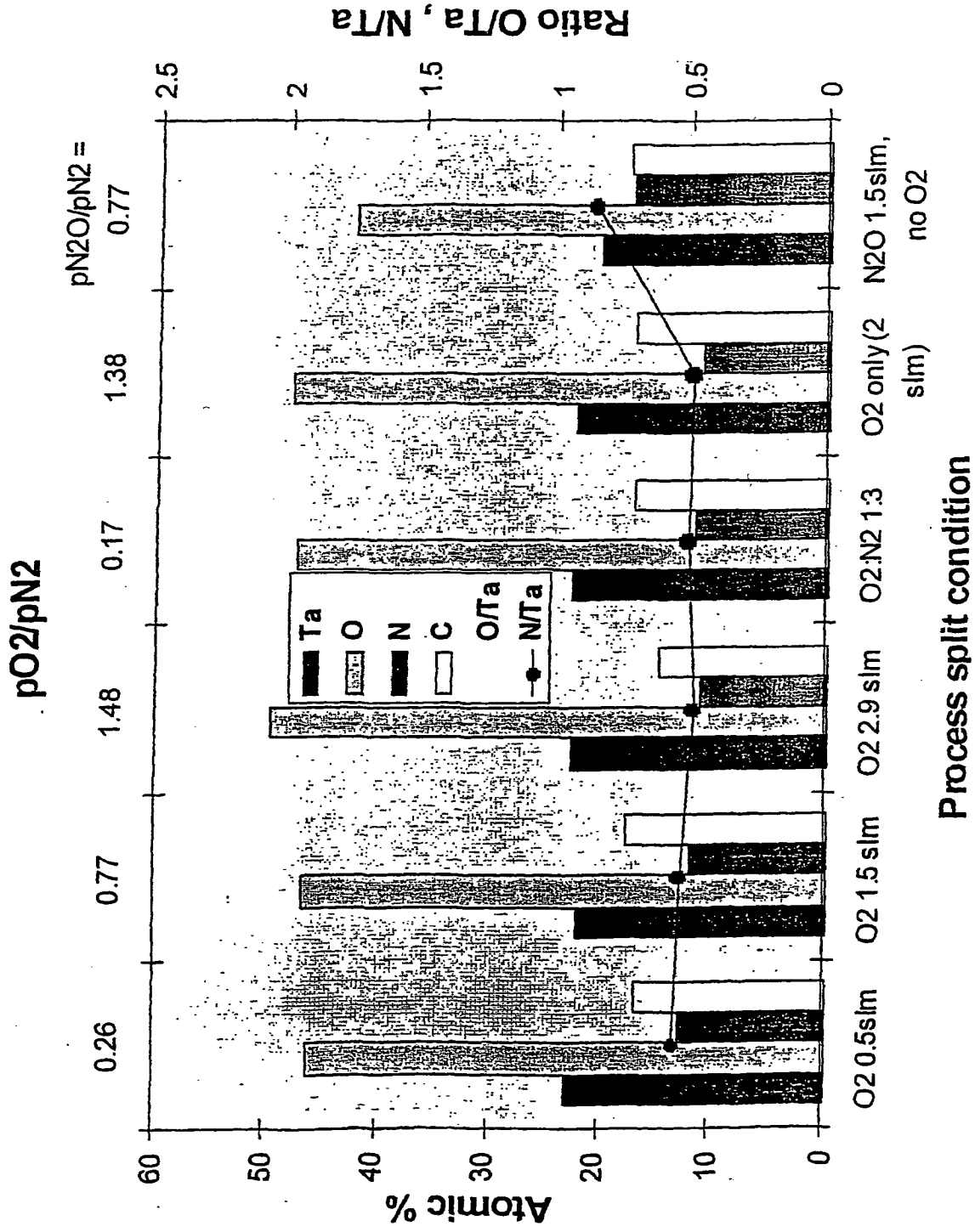

Fig. 7B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/28061

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : C23C 16/40
US CL : 438/381, 785; 427/255.31, 79
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 438/381, 785; 427/255.31, 79

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,037,003 A (GORDON et al) 14 March 2000 (14.03.2000), col. 2, lines 7-17.	1-11
Y	Tabuchi, T. et al., "Application of Penta-Di-Methyl-Amino-Tantalum to a Tantalum Source in Chemical Vapor Deposition of Tantalum Oxide Films", Japanese Journal of Applied Physics, Vol. 30, No. 11B, November 1991, pages L1974-L1977, especially page L1974.	1-11
Y	Chiu et al., "Deposition of Tantalum Nitride Thin Films from Ethylimidotantalum Complex", Journal of Materials Science Letters, Volume 11, 1992, pages 96-98, especially page 96	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 November 2001 (01.11.2001)	28 NOV 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Timothy H Meeks Jean Proctor Paralegal Specialist Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)